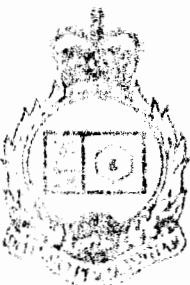


30



ANALYTICAL PROCEDURES FOR LIQUID CATION EXCHANGE CELLS

by

G. Verville and P. Powell

AD-A142 004



DEFENCE RESEARCH ESTABLISHMENT OTTAWA
TECHNICAL NOTE 83-26

Approved for public release; distribution is unlimited.
This document contains neither recommendations nor conclusions of the
Department of National Defence. It has been reviewed and approved
for external release by the DND Public Affairs Directorate.

April 1984
OTTAWA



National
Defence
Défense
nationale

RAPID ELECTROLYTE EXCHANGE PROCEDURES FOR 22 AH NICKEL-CADMIUM CELGARD CELLS

by

G. Verville and P. Powell
Chemical Sources Section
Energy Conversion Division

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/ _____	
Availability Codes	
Air Mail and/or	<input type="checkbox"/>
Dist	Special
A-1	

DTIC

DEFENCE RESEARCH ESTABLISHMENT OTTAWA
TECHNICAL NOTE 83-25

PCN
25A10

April 1984
Ottawa

This document has been approved
for public release and sale; its
distribution is unlimited.

ABSTRACT

State-of-the-health analysis of Nickel-Cadmium aircraft batteries rejected as being unsatisfactory by CF bases has shown that most of the problems encountered can be related to the fact that the KOH concentration in the cells is too low and/or the carbonate concentration is too high.

Exchange of electrolyte restored the performances of the cells but is time consuming, one to two weeks for a battery using the charge-KOH exchange-discharge procedure.

The present technical note describes some of the tests performed and a procedure for rapidly exchanging the electrolyte in 22 AH Nickel-Cadmium Aircraft Celgard cells,

RÉSUMÉ

Une analyse des batteries usagées nickel-cadmium d'aéronef a montré que la baisse de performances observée par les forces armées canadiennes pouvait être attribuée dans une large part à une concentration trop faible en potasse et/ou à une concentration trop élevée en carbonate dans l'électrolyte.

Dans plusieurs cas, un échange d'électrolyte redonna les performances attendues. Toutefois cet échange d'électrolyte prend énormément de temps; une à deux semaines selon la méthode de la charge-échange KOH-décharge de la batterie.

Le présent document offre une nouvelle méthode d'échange de l'électrolyte d'une durée de quelques heures et décrit les tests effectués avec des prototypes. La méthode décrite a été adaptée aux batteries d'aéronef d'une capacité de 22 AH, montées avec des séparateurs "celgard".

TABLE OF CONTENTS

	<u>Page</u>
<u>ABSTRACT/RESUME</u>	iii
<u>TABLE OF CONTENTS</u>	v
<u>FIGURE CAPTIONS</u>	vii
<u>INTRODUCTION</u>	1
<u>BASIC PROCESS</u>	1
<u>EFFICIENCY OF THE PROCESS</u>	2
<u>SIX CELL PROTOTYPE</u>	2
<u>ELECTROLYTE EXCHANGE PROCEDURES FOR 22 AH NICKEL-CADMUM CELGARD CELLS</u>	3
<u>Equipment Required</u>	3
<u>Procedure and Operations</u>	4
<u>Vacuum Leakage Problems</u>	4
<u>Turbid Electrolyte</u>	5
<u>CONCLUSION</u>	5
<u>REFERENCES</u>	5

LIST OF ILLUSTRATIONS

Figure 1. Exchange of Electrolyte Apparatus: Single Cell Prototype.

Figure 2. Efficiency of Mixing During the First Hour.
1 Discharged Cells
2 Charged Cells

Figure 3. Exchange of Electrolyte Apparatus: Six Cell Prototype.

Figure 4. Lowering of KOH Concentration in Cells After the Exchange of Electrolyte.
▲ Water and KOH Exchange Cells
• KOH Exchange Cells

Figure 5. Example of Turbidity in Cell Electrolyte.

INTRODUCTION

During recent years, DREO/ECD personnel have conducted state-of-the-health analysis of Nickel-Cadmium cells rejected as being unsatisfactory by CF bases. Experiments have shown that most of the problems encountered result from the KOH concentration in the cells being too low and/or the carbonate concentration being too high (1). Experiments have also shown that after an exchange of electrolyte that brings the KOH and the carbonate concentration within the range suggested in (2), the performance of the cells is restored.

In the past, the cells that were built with a cellophane separator and used for cranking applications lasted less than three years so the cells were often rejected before the need of exchanging the electrolyte appeared. Celgard cells last much longer and it is expected that the electrolyte will need to be exchanged after 3-5 years of field service.

Exchange of electrolyte has always been time consuming (one to two weeks for a battery using the charge-KOH exchange-discharge procedures). DREO/ECD has developed procedures (3,4,5) that reduce this time to about two days. Improvements of the techniques (6) suggest that a complete exchange of electrolyte in a battery can be accomplished within one working day.

The present Technical Note describes some of the tests performed and suggests a procedure for exchanging the electrolyte in 22 AH Nickel-Cadmium Celgard cells. These techniques should not be used for the Nickel-Cadmium cellophane cells still in use in the CF because the application and the release of the vacuum during the process might damage the cellophane separator and promote the formation of internal short-circuits.

BASIC PROCESS

The schematic diagram and details of the required equipment for electrolyte exchange have been covered in (5,6) and will be briefly reviewed for illustrative purposes. Figure 1 shows an exchange of electrolyte apparatus in the simplest configuration. A cell with contaminated electrolyte is mounted on a shaft which can be rotated to position the cell right-side-up or inverted as desired. A modified vent cap and tubing connector make connection to tubing which leads into the bottom region of a volumetric flask referred to as the "Exchange Flask". This flask is linked to a vacuum line. The vacuum is applied and released by a solenoid valve operated by a cycling timer. When the timer causes the vacuum to be applied a quantity of the electrolyte (30-40 ml) from the cell is withdrawn into the exchange flask. It mixes with the much larger quantity of fresh electrolyte causing only small changes in composition. When the vacuum is released on the second

part of the cycle, the electrolyte in the exchange flask flows back into the cell. This mixes in the cell with the remaining contaminated electrolyte and the process is repeated. Eventually the electrolyte in the exchange flask and the cell are of equal concentration. However due to the relative volumes when the process was started the quality in the cells is now much higher than it was originally. The major advantage of this process over the charge-exchange KOH-discharge process is that this process does not tie up, for extended periods of time, the charge-discharge equipment and it does not interfere with the daily battery shop duties.

EFFICIENCY OF THE PROCESS

In order to measure the process efficiency and reproducibility from cell to cell, the electrolyte of four cells in the charged state and four cells in the discharged state has been changed using the prototype shown in Figure 1. The initial KOH concentration in the cells was in the range 29-32% KOH and 500 ml of water was added in the exchange flask each time the electrolyte in a cell was exchanged. The vacuum mixing cycles were 18 seconds "vacuum on" 12 seconds "vacuum off". The KOH concentration after 24 hours of mixing was considered as 100% mixing. The percent of mixing with time was calculated according to the formula:

$$\% \text{ mixing} = \frac{C_t}{C_{24}} \quad (1)$$

where C_t = % KOH in the exchange flask at a given time and
 C_{24} = % KOH after 24 hours of mixing.

The data obtained during the first hour of mixing are presented in Figure 2. It appears that the mixing in the charged cells took place more rapidly than in the discharged cells. This is consistent with the fact that the charged cells have about 30 ml of "free electrolyte" available at the beginning of mixing and that the plates in the charged state have a more open structure. The vertical bars represented the range of data obtained with four different cells. From the height of the bars one can see that the reproducibility of mixing is also better with the charged cells. After one hour of mixing, 80% of mixing is completed in the charged cells compared with 65% with cells in the discharged state. However for safety reasons during the manipulation of the cells, it is not advised to exchange the electrolyte while the cells are in the charged state and work has been pursued with cells in the discharged state.

SIX CELL PROTOTYPE

DREO/ECD has developed a prototype that allows the exchange of electrolyte in six cells at a time (Figure 3). The prototype has a four litre exchange flask and has been used to establish the working procedures to exchange electrolyte in a battery shop.

Water exchange treatments have been conducted in order to try to minimize the difference in KOH concentration from cell to cell prior to the exchange of KOH electrolyte. Six cells containing from 20% to 30% KOH electrolyte were vacuum-cycled for a ten minute period with 2,500 ml of water in the exchange flask. At the end of the 10 minute period, the 2,500 ml of electrolyte was dumped and 2500 ml of fresh water was added to the exchange flask and mixed for another ten minute period. This treatment reduced the KOH concentration to 5% in each of the six cells. After the water exchange treatment, 3,000 ml of 37% KOH (500 ml/cell) were added to the exchange flask and the cells were vacuum cycled for one hour.

Another set of six cells with from 20% to 30% KOH electrolyte were exempted from the water treatment and were vacuum cycled for one hour with 3,000 ml of 37% KOH in the exchange flask. The KOH concentration was analysed immediately after the treatment and during the following days while both sets of cells were at rest at room temperature.

After the exchange of electrolyte, the cells that received the water treatment showed an average of $28.5 \pm 0.7\%$ KOH and the cells without water treatment $35.2 \pm 0.3\%$ KOH. The difference from cell to cell was more significant with the cells that had received the water treatment. This difference further increased as the cells were left at rest. Figure 4 illustrates the data of the cells with the highest and the lowest KOH concentration for each set of cells. At rest, the cells that received the water treatment decreased in KOH concentration by an average of 1.5% KOH while the cells without the water treatment decreased in KOH concentration by an average of 0.5% KOH. It appears that the water treatment prior to the exchange of KOH electrolyte does not offer any advantages and in fact creates some additional problems in terms of reproducibility from cell to cell. For these reasons the water treatment has been abandoned.

In further experiments, reproducible results were obtained by introducing in the exchange flask 2,400 ml of 32% KOH (400 ml/cell) and vacuum mixing for one hour. The details of the procedure will be explained in the following paragraphs.

ELECTROLYTE EXCHANGE PROCEDURES FOR 22 AH NICKEL-CADMIUM CELGARD CELLS

Equipment Required

- Six cell holder (BBQ type), as illustrated in Figure 3.
- Vacuum facilities: primary vacuum pump (Model No. 0211-V45N-68CX manufactured by Cast or the equivalent) or building vacuum facilities.
- 4,000 ml exchange flask.
- Magnetic stirrer for mixing the electrolytes in the exchange flask.
- 32% KOH solution.

- Solenoid valve (manufactured by ASCO, cat-no. 8329A44N, 117 VAC, orifice 1/8", pipe 1/8").
- Adjustable CAM operated timer switch with 30 second cycle time. (Industrial Timer Corp).
- Tygon tubing with 1/4" bore and 1/16" wall thickness or equivalent.
- Modified vent caps (3,4).

Procedure and Operations

Six 22 AH discharged cells are tightly secured in the rotatable cell holder. Each cell has a modified vent cap which is connected via tubing to the 4,000 ml exchange flask. The exchange flask sits on a magnetic stirrer which is used to mix the electrolyte. The exchange flask is filled with 32% KOH (400 ml/cell). The vacuum pump is turned on and the cycling timer is switched on. The suggested cycling mode is 18 seconds "vacuum on" and 12 seconds "vacuum off". Cells are allowed to fill in the upright position for about two minutes. The cell holder is then inverted and the "exchange of electrolyte" operations are left on for at least one hour. At the end of the one hour period, the KOH concentration in each of the cells should be around $30 \pm 1.0\%$ (tests have been done with cells having a KOH initial concentration of $23 \pm 1\%$ KOH). As the mixing is not completed after one hour of mixing, a further decrease of about 0.5% KOH is expected. The KOH concentration ends up within the range specified in (2). At the end of the "exchange of electrolyte" treatment the excess of electrolyte in each cell must be emptied prior to charging and the level of electrolyte must be adjusted according to the procedures in (2) at the end of charge.

The volume of KOH electrolyte (400 ml/cell) in the exchange flask has been selected to cover a wide range of cell electrolyte concentrations. The total volume has been selected such that any carbonate concentration in the cells will be reduced or diluted by a factor of about four. For instance, cells with electrolyte in the range 15-30% KOH and carbonate up to 15% should finish after the exchange of electrolyte, with electrolyte in the range suggested in (2).

The suggested exchange procedures require the manipulation of large quantities of KOH electrolyte and it is recommended that safety goggles be worn during the operation. The development of a prototype for the exchange of more than six cells at a time required the use of volumes of electrolyte too large for safe handling in a battery maintenance shop and has been abandoned.

Vacuum Leakage Problems

Vacuum leakages can be detected by a constant bubbling in the exchange flask while the vacuum is applied. As some air is left in the cells, bubbling in the exchange flask is normal during the first exchange of electrolyte cycles but should cease. If after two minutes of cycling bubbling persists, a vacuum leakage is indicated. It has been observed that leakages commonly

occurs at the vent cap connection. The wrapping of teflon tape around the vent caps should overcome most of the leakage problems encountered. If leakages persist, the cells responsible for the leakage must be discarded from the exchange treatment and replaced.

Turbid Electrolyte

It is not advised to use this process for cells having "muddy" electrolyte". The electrolyte in each cell should be inspected for turbidity prior to the exchange of electrolyte. Samples of electrolyte may be taken from each cell with a syringe while the battery is in overcharge and gassing, and placed in test tubes for observation. Figure 5 shows examples of electrolyte from cells which had seen extensive use. They are arranged to show the wide range of turbidity which may be found. The two test tubes shown at the right hand end contain pure electrolyte for reference purposes. The two samples at the left are extremely "muddy". Cells having "muddy" electrolyte should be discarded, they will contaminate the electrolyte of the other cells with solid particles during the "exchange of electrolyte" process. It is likely that cells with large quantities of material in the electrolyte, and by inference in the separator materials, would develop short circuits in the near future and should be removed from service.

CONCLUSION

DREO/ECD has developed a prototype that allows the exchange of KOH electrolyte in 22 AH Nickel-Cadmium Celgard Cells within a working day period. The major advantage of this process over the charge-exchange KOH- discharge process is that the new process requires little charge-discharge equipment time and does not interfere with daily battery shop duties. The prototype and the suggested procedures should be evaluated at AMDU in the near future and if found satisfactory should be introduced into CF battery shops that handle 22 AH celgard cells.

REFERENCES

1. DREO 3625A-2 (ECD) dated 30 June 1982.
2. T.O. C-93-155-000/MN-000.
3. K. Feldman and R.M. Hayashi, Nickel-Cadmium Aircraft Batteries: Rapid Electrolyte Exchange Technique. DREO Tech. Note 77-8.
4. K. Feldman. Additional Information to Technical Note 77-8, on Rapid Electrolyte Exchange Technique, DREO Memorandum No. 43/79.
5. K. Feldman and G. Verville, Vacuum Mixing-Washing Technique for Nickel-Cadmium Aircraft Cells. DREO Memorandum No. 2/81.
6. K. Feldman, R.J. Charest, G. Verville and J.L. Lackner, Rejuvenation of Nickel-Cadmium Aircraft Battery Electrolyte, Canadian Patent Application No. 396,358.

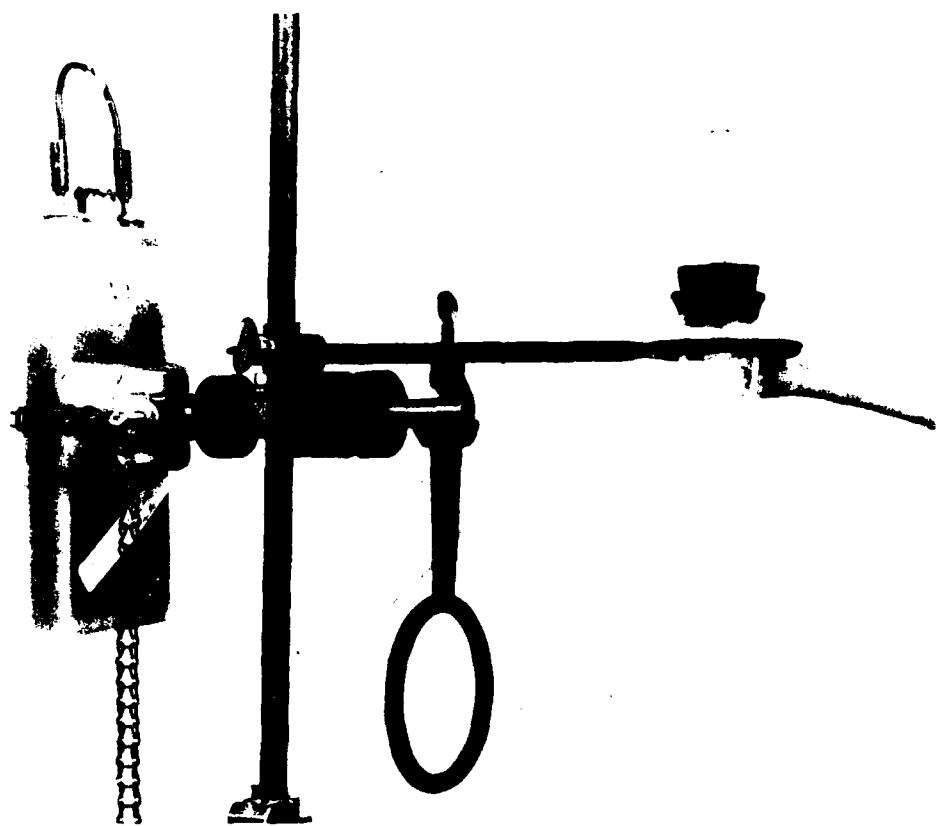


Figure 1. Exchange of Electrolyte Apparatus:
Single Cell Prototype.

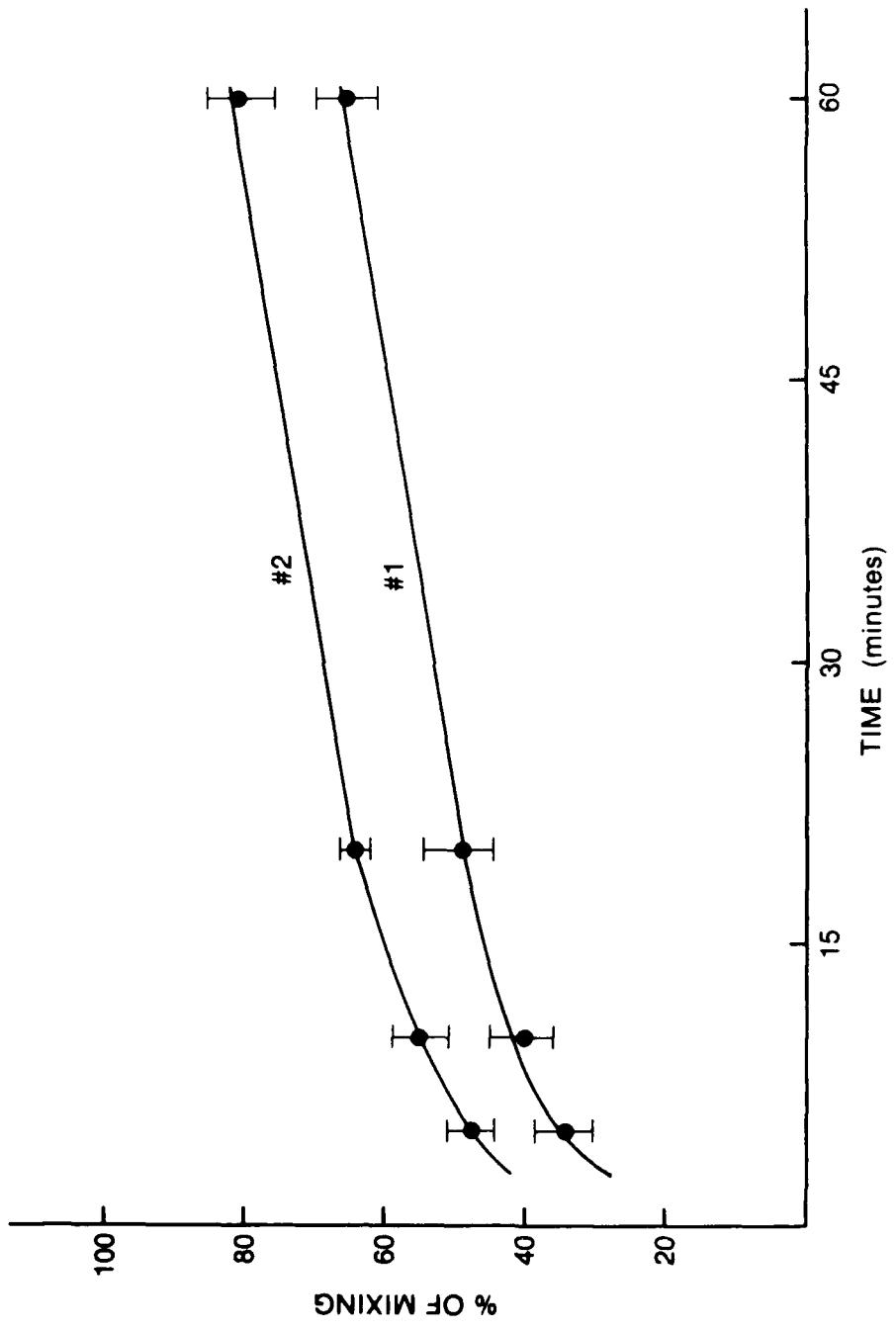


Figure 2. Efficiency of Mixing During the First Hour.
1 Discharged Cells.
x 2 Charged Cells.

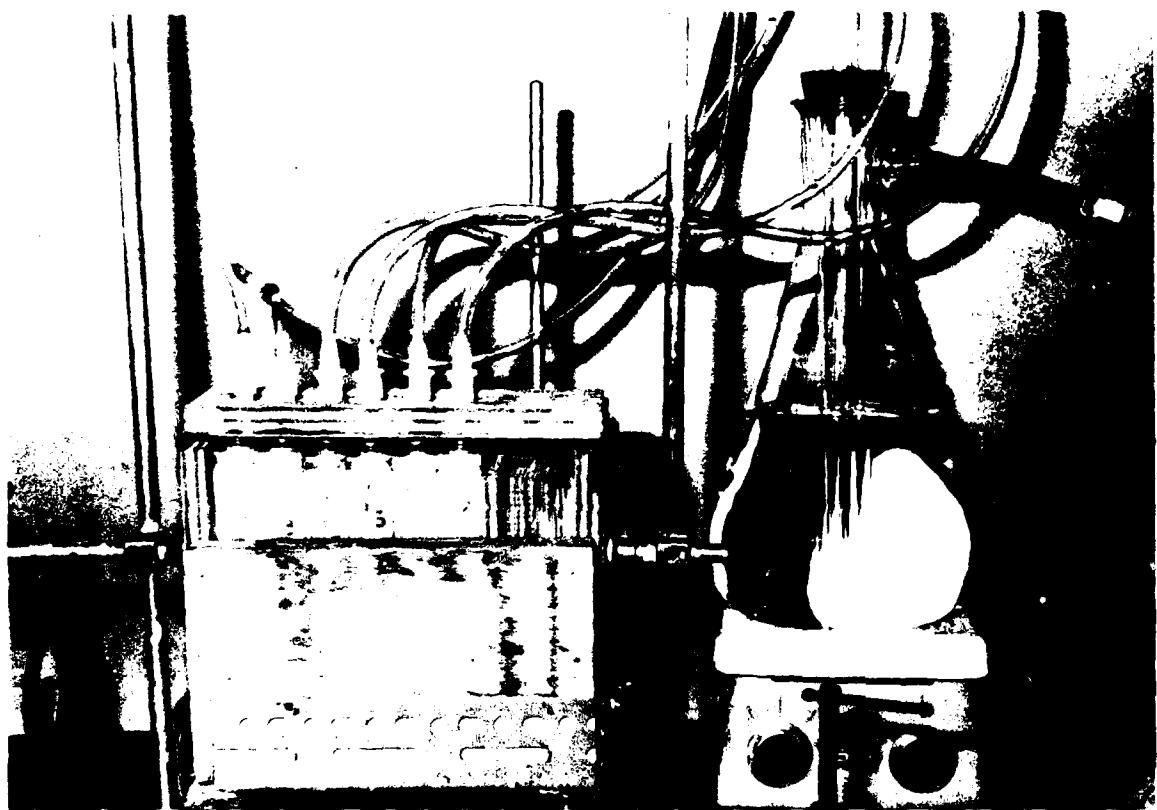


Figure 3. Exchange of Electrolyte Assembly of Six Cell Prototype.

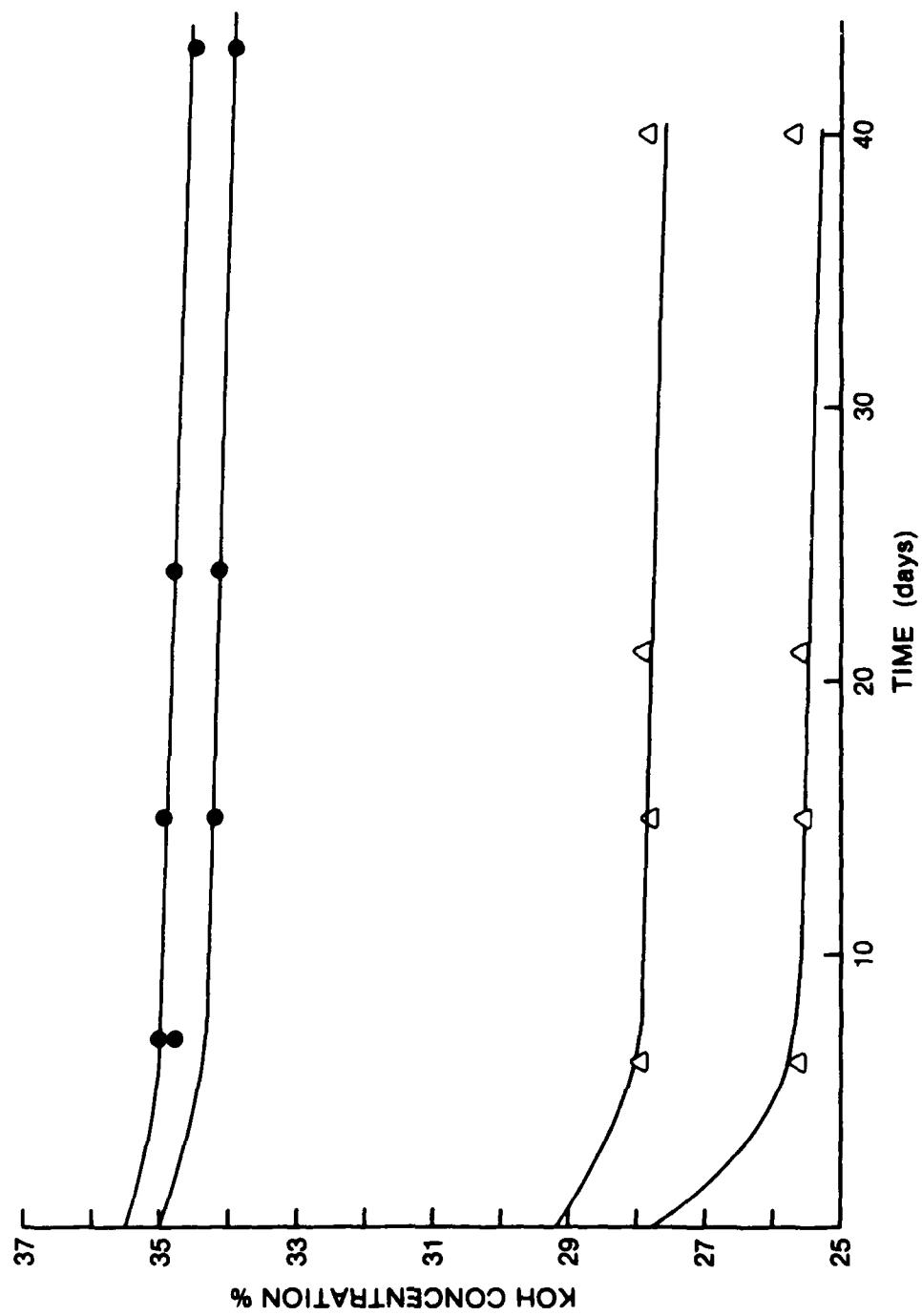


Figure 4. Lowering of KOH Concentration in Cells After the Exchange of Electrolyte.
Δ Water and KOH Exchange Cells
● KOH Exchange Cells

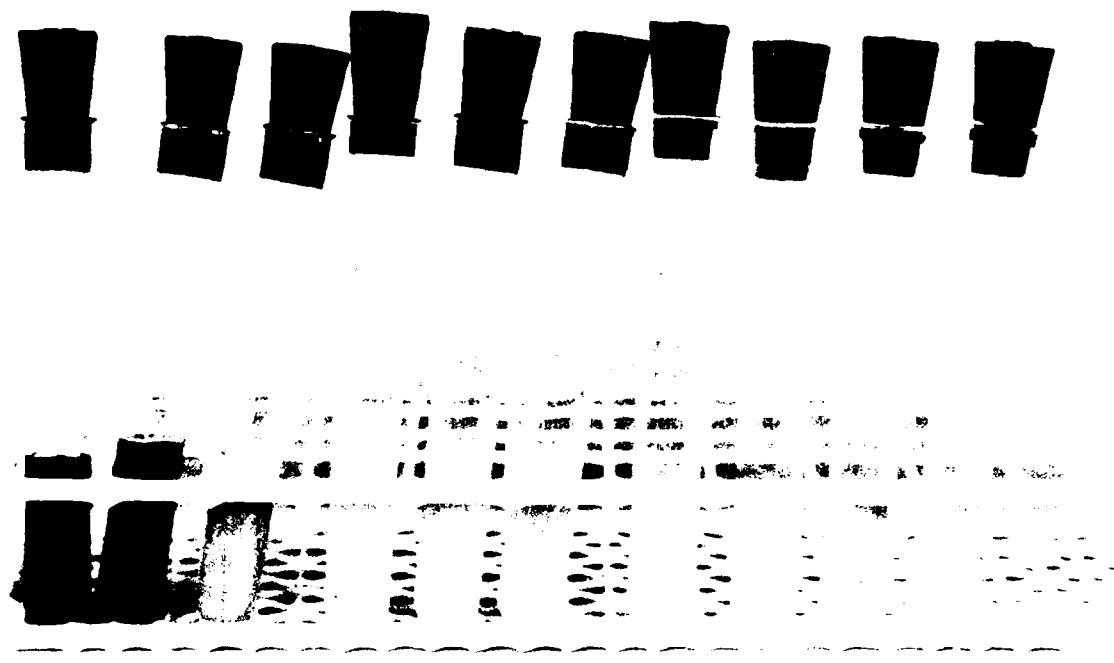


Figure 5. Example of Turbidity in Cell Electrolyte.

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall document is classified)

1 ORIGINATING ACTIVITY DEFENCE RESEARCH ESTABLISHMENT OTTAWA Department of National Defence Ottawa, Ontario, K1A 0Z4, Canada		2a DOCUMENT SECURITY CLASSIFICATION Unclassified
		2b GROUP
3 DOCUMENT TITLE RAPID ELECTROLYTE EXCHANGE PROCEDURES FOR 22 AH NICKEL-CADMUM CELGARD CELLS (U)		
4 DESCRIPTIVE NOTES (Type of report and inclusive dates) Technical Note		
5 AUTHOR(S) (Last name, first name, middle initial) Verville, G. and Powell, P.		
6 DOCUMENT DATE April 1984	7a TOTAL NO OF PAGES 10	7b NO OF REFS 6
8a PROJECT OR GRANT NO 25A10	9a ORIGINATOR'S DOCUMENT NUMBER(S) DREO TN 83-25	
8b CONTRACT NO	9b OTHER DOCUMENT NO (S) (Any other numbers that may be assigned this document)	
10 DISTRIBUTION STATEMENT Unlimited		
11 SUPPLEMENTARY NOTES	12 SPONSORING ACTIVITY DREO	
13 ABSTRACT State-of-the-health analysis of Nickel-Cadmium aircraft batteries rejected as being unsatisfactory by CF bases has shown that most of the problems encountered can be related to the fact that the KOH concentration in the cells is too low and/or the carbonate concentration is too high. Exchange of electrolyte restored the performances of the cells but is time consuming, one to two weeks for a battery according to the charge-KOH exchange-discharge procedure. The present technical note describes some of the tests performed and a procedure for rapidly exchanging the electrolyte in 22 AH Nickel-Cadmium Aircraft Celgard Cells.		

UNCLASSIFIED

Security Classification

KEY WORDS

Nickel-Cadmium Celgard Cells
 Nickel-Cadmium Aircraft Batteries
 KOH Electrolyte Contamination
 Rapid Electrolyte Exchange Technique

INSTRUCTIONS

1. ORIGINATING ACTIVITY Enter the name and address of the organization issuing the document.
- 2a. DOCUMENT SECURITY CLASSIFICATION Enter the overall security classification of the document including special warning terms whenever applicable.
- 2b. GROUP Enter security reclassification group number. The three groups are defined in Appendix 'M' of the DRB Security Regulations.
3. DOCUMENT TITLE Enter the complete document title in all capital letters. Titles in all cases should be unclassified. If a sufficiently descriptive title cannot be selected without classification, show title classification with the usual one capital-letter abbreviation in parentheses immediately following the title.
4. DESCRIPTIVE NOTES Enter the category of document, e.g. technical report, technical note or technical letter. If appropriate, enter the type of document, e.g. interim, progress, summary, annual or final. Give the inclusive dates when a specific reporting period is covered.
5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the document. Enter last name, first name, middle initial. If military, show rank. The name of the principal author is an absolute minimum requirement.
6. DOCUMENT DATE Enter the date (month, year) of Establishment approval for publication of the document.
- 7a. TOTAL NUMBER OF PAGES The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information
- 7b. NUMBER OF REFERENCES Enter the total number of references cited in the document
- 8a. PROJECT OR GRANT NUMBER If appropriate, enter the applicable research and development project or grant number under which the document was written.
- 8b. CONTRACT NUMBER If appropriate, enter the applicable number under which the document was written.
- 9a. ORIGINATOR'S DOCUMENT NUMBER(S) Enter the official document number by which the document will be identified and controlled by the originating activity. This number must be unique to this document.
- 9b. OTHER DOCUMENT NUMBER(S) If the document has been assigned any other document numbers (either by the originator or by the sponsor), also enter this number(s).
10. DISTRIBUTION STATEMENT Enter any limitations on further dissemination of the document, other than those imposed by security classification, using standard statements such as
 - (1) "Qualified requesters may obtain copies of this document from their defence documentation center."
 - (2) "Announcement and dissemination of this document is not authorized without prior approval from originating activity"
11. SUPPLEMENTARY NOTES Use for additional explanatory notes.
12. SPONSORING ACTIVITY Enter the name of the departmental project office or laboratory sponsoring the research and development. Include address.
13. ABSTRACT Enter an abstract giving a brief and factual summary of the document, even though it may also appear elsewhere in the body of the document itself. It is highly desirable that the abstract of classified documents be unclassified. Each paragraph of the abstract shall end with an indication of the security classification of the information in the paragraph (unless the document itself is unclassified) represented as (TS), (SI), (CI), (RI), or (U).

The length of the abstract should be limited to 20 single spaced standard typewritten lines, 7½ inches long
14. KEY WORDS Key words are technically meaningful terms or short phrases that characterize a document and could be helpful in cataloging the document. Key words should be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context.